

RESERVE  
PATENT SPECIFICATION

415,172



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PROVISIONAL SPECIFICATION.

Improvements in the Catalytic Oxidation of Ketones.

I, JAMES YATE JOHNSON, a British Subject, of 47, Lincoln's Inn Fields, in the County of London, Gentleman, do hereby declare the nature of this invention 5 (which has been communicated to me from abroad by I. G. Farbenindustrie Aktiengesellschaft, of Frankfort-on-Main, Germany, a Joint Stock Company organized under the Laws of Germany)

10 to be as follows:—

My foreign correspondents have found that cycloaliphatic ketones can be catalytically oxidised to di-carboxylic acids which are obtained in very good yields by carrying out the reaction in the liquid phase by means of oxygen or a gas containing oxygen, such as air or air enriched in oxygen, for example containing 50 per cent of oxygen, in the presence of oxidation catalysts.

15 The reaction may be carried out at atmospheric pressure or at a pressure above atmospheric pressure, provided the formation of explosive mixtures is avoided; the partial pressure of the oxygen should, accordingly, not exceed about 5, preferably about 4 atmospheres. Thus for example, when air is employed, the reaction may be carried out at a pressure up to about 20 atmospheres, whereas a pressure up to about 5 atmospheres may be employed when oxygen is used as the oxidising agent.

20 As examples of ketones which may be subjected to the oxidation according to the present invention there may be mentioned cyclopentanone, cyclohexanone, methyl-cyclohexanone, and like ketones.

25 Cyclopentanone yields glutaric acid, cyclohexanone yields adipic acid, and methylcyclohexanone yields methyl adipic acid.

30 The oxidation catalysts which may be employed for carrying out the present invention comprise solid metals capable of forming compounds with different valencies and having an atomic weight between about 50 and about 200, such as for example vanadium, chromium, manganese, iron, cobalt, nickel, copper, 35 molybdenum, the rare earths such as cerium, praseodymium, neodymium, lanthanum, samarium and the terbium earths, tungsten, platinum, iridium and

osmium and gold. These metals may be added to the reaction mixture in the metallic, finely divided state, preferably in the form of powders, or also in the form of their oxides, carbonates, chlorides, sulphates, or carboxylates such as formiates, acetates, propionates, stearates, oleates, tartrates or also in the form of their enolates, such as acetyl acetonates. Among these catalysts manganese and cobalt are especially useful, 40 preferably in the form of their formates, acetates or acetylacetones. Mixtures of several of these catalysts may also be employed, for example a mixture of cobalt and manganese in the form of their acetates and/or acetylacetones.

Very small amounts of the aforesaid oxidation catalysts are sufficient for carrying out the reaction. Thus, for example about 0.01 per cent, by weight of the ketone, of the catalyst is sufficient for a marked oxidation; usually, the catalysts are, however, used in an amount of from about 0.1 to about 1 per cent by weight of the ketone, quantities such as 2, 3, 5 or 10 per cent, or even more, being, however, 45 also used if so desired.

Very small amounts of the aforesaid oxidation catalysts are sufficient for carrying out the reaction. Thus, for example about 0.01 per cent, by weight of the ketone, of the catalyst is sufficient for a marked oxidation; usually, the catalysts are, however, used in an amount of from about 0.1 to about 1 per cent by weight of the ketone, quantities such as 2, 3, 5 or 10 per cent, or even more, being, however, 50 also used if so desired.

As stated above, the oxidation is carried out in the liquid phase. This means that the ketones are oxidised in the liquid or dissolved state. Solvents which may be employed for dissolving the ketones are for example carboxylic acids containing from 1 to 3 carbon atoms, such as formic acid, acetic acid and propionic acid, and methyl or ethyl esters of these acids. Halogenated hydrocarbons such as carbon tetrachloride or chlorobenzene may also be employed as the solvents. All these solvents are practically inert to the oxidation and capable of dissolving the initial ketones. Glacial acetic acid is, however, the preferred solvent to be employed. The use of acetic or formic acid is especially advantageous when the catalyst is employed in the metallic state, because the metal is then readily dissolved. In order to initiate the reaction it is preferable to add a small amount, such as 1 per cent by weight of the ketone, of acetic acid or another of the aforesaid acids, also when the reaction is carried out in the absence of solvents.

The reaction is generally carried out at temperatures between about 50° and about 120° Centigrade, preferably between about 75° and 105° Centigrade. It is usually carried out by heating the reaction mixture to the aforesaid temperatures in order to initiate the reaction; after some time heating is no longer necessary since the heat evolved maintains the mixture at the reaction temperature. Sometimes cooling may even become necessary in order to avoid too complete oxidation.

The oxidation may be effected for example by blowing oxygen, or gaseous mixtures containing oxygen, such as air, into the liquid or dissolved ketone heated to about boiling point of the ketone or of the solvent to which ketone or solution thereof of an oxidation catalyst has been added and which is situated in a vertical long cylindrical vessel provided with a reflux condenser. It is advantageous to disperse the oxidising gas as finely as possible, as for example by employing finely porous glass filter plates (fritted glass particles) and filler bodies, such as shavings or, especially bodies of the kind known as Raschig rings. The reaction vessel is constructed from materials resistant to the components of the reaction and, if necessary, pressure-tight. Such materials are for example ceramic masses, glass or metal alloys such as chrome-nickel steels, or nickel alloys free from iron. Similarly, the filler bodies may be made from the same resisting materials. It is advantageous to add a small amount of an acid, preferably acetic acid, to the ketone at the start, since in this case the reaction commences immediately.

When carrying out the reaction with ketones having a boiling point below the reaction temperature working under increased pressure is necessary in order to keep the ketone in the liquid phase. It is, however, also possible in this case to dissolve the ketone in a solvent having a higher boiling point, such as glacial acetic acid, in which case the reaction may also be carried out at atmospheric pressure, the use of an increased pressure being, however, also possible.

The process proceeds in a particularly advantageous manner when acetic acid together with the catalyst is first introduced into the oxidation vessel, the ketone to be oxidised being introduced gradually into the acetic acid solution or other dispersion while simultaneously leading in oxygen or air. Working in

the last-mentioned manner has the advantage that the process may be carried out at temperatures up to the boiling point of the acid employed for dispersing the catalyst without the employment of increased pressure. At the same time the yield is especially favourable. It is preferable to introduce the ketone, the solvent if such be employed, and the catalyst into the vessel and to carry out the oxidation as a batch process.

The waste gas formed during the oxidation contains but a little carbon dioxide and a little aldehyde, such as acetaldehyde which is formed as an intermediate product in the reaction; the gas may be used for further oxidations, if desired, after washing out the aldehyde and the carbon dioxide, for example with the aid of an aqueous solution of a caustic alkali, such as caustic soda or caustic potash, if desired after separating the aldehyde by cooling.

The following Examples will further illustrate the nature of this invention but the invention is not restricted to these Examples.

#### EXAMPLE 1.

A mixture of 98 grams of cyclohexanone with 100 grams of glacial acetic acid and 0.1 gram of manganese acetate is introduced into the vessel described in Example 1. After heating the vessel to about 100° Centigrade a current of air is introduced through the glass filter at the rate of 25 litres per hour. After 5 hours the oxidation is interrupted and the unaltered cyclohexanone is distilled off together with the acetic acid, the distillate being then subjected again to oxidation. Adipic acid is thus obtained in a yield corresponding to 80 per cent of the cyclohexanone employed.

#### EXAMPLE 2.

A solution of 112 grams of methyl cyclohexanone in 100 grams of glacial acetic acid is oxidised in the manner described in Example 3, after the addition of 0.1 gram of manganese acetate, the reaction temperature being, however, 80° Centigrade. The yield in methyl adipic acid is 74 per cent calculated on the methyl cyclohexanone employed.

Dated this 17th day of March, 1933.

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## COMPLETE SPECIFICATION.

## Improvements in the Catalytic Oxidation of Ketones.

I, JAMES YATE JOHNSON, a British Subject, of 47, Lincoln's Inn Fields, in the County of London, Gentleman, do hereby declare the nature of this invention (which has been communicated to me from abroad by I. G. Farbenindustrie Aktiengesellschaft, of Frankfort-on-Main, Germany, a Joint Stock Company organized under the Laws of Germany) and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

My foreign correspondents have found that cycloaliphatic ketones can be catalytically oxidised to dicarboxylic acids which are obtained in very good yields by carrying out the reaction in the liquid phase by means of oxygen or a gas containing oxygen, such as air or air enriched in oxygen, for example containing 50 per cent of oxygen, in the presence of oxidation catalysts.

The reaction may be carried out at atmospheric pressure or at a pressure above atmospheric pressure, provided the formation of explosive mixtures is avoided; the partial pressure of the oxygen should, accordingly, not exceed about 5, preferably about 4 atmospheres. Thus for example, when air is employed, the reaction may be carried out at a pressure up to about 20 atmospheres, whereas a pressure up to about 5 atmospheres may be employed when oxygen is used as the oxidising agent.

As examples of ketones which may be subjected to the oxidation according to the present invention there may be mentioned cyclopentanone, cyclohexanone, methyl-cyclohexanone and like ketones. Cyclo-pentanone yields glutaric acid, cyclohexanone yields adipic acid, and methylcyclohexanone yields methyl adipic acid.

The oxidation catalysts which may be employed for carrying out the present invention comprise solid metals capable of forming compounds with different valencies and having an atomic weight between about 50 and about 200, such as for example vanadium, chromium, manganese, iron, cobalt, nickel, copper, molybdenum, the rare earths such as cerium praseodymium, neodymium, lanthanum, samarium and the terbium earths, tungsten, platinum, iridium and osmium and gold. These metals may be added to the reaction mixture in the metallic, finely divided state, preferably in the form of powders, or also in the form of their oxides, car-

bonates, chlorides, sulphates, or carboxylates such as formates, acetates, propionates, stearates, oleates, tartrates or also in the form of their enolates, such as acetyl acetones. Among these catalysts manganese and cobalt are especially useful, preferably in the form of their formates, acetates or acetylacetones. Mixtures of several of these catalysts may also be employed, for example a mixture of cobalt and manganese in the form of their acetates and/or acetylacetones.

Very small amounts of the aforesaid oxidation catalysts are sufficient for carrying out the reaction. Thus, for example about 0.01 per cent, by weight of the ketone, of the catalyst is sufficient for a marked oxidation; usually, the catalysts are, however, used in an amount of from about 0.1 to about 1 per cent by weight of the ketone, quantities such as 2, 3, 5, or 10 per cent, or even more, being, however, also used if so desired.

As stated above, the oxidation is carried out in the liquid phase. This means that the ketones are oxidised in the liquid or dissolved state. Solvents which may be employed for dissolving the ketones are for example carboxylic acids containing from 1 to 3 carbon atoms, such as formic acid, acetic acid and propionic acid, and methyl or ethyl esters of these acids. Halogenated hydrocarbons such as carbon tetrachloride or chlorobenzene may also be employed as the solvents. All these solvents are practically inert to the oxidation and capable of dissolving the initial ketones. Glacial acetic acid, is, however, the preferred solvent to be employed. The use of acetic or formic acid is especially advantageous when the catalyst is employed in the metallic state, because the metal is then readily dissolved. In order to initiate the reaction it is preferable to add a small amount, such as 1 per cent by weight of the ketone, of acetic acid or another of the aforesaid acids, also when the reaction is carried out in the absence of solvents.

The reaction is generally carried out at temperatures between about 50° and about 120° Centigrade, preferably between about 75° and 105° Centigrade. It is usually carried out by heating the reaction mixture to the aforesaid temperatures in order to initiate the reaction: after some time heating is no longer necessary since the heat evolved maintains the mixture at the reaction temperature. Sometimes cooling may even become necessary in order to avoid too complete oxidation.

The oxidation may be effected for example by blowing oxygen, or gaseous mixtures containing oxygen, such as air, into the liquid or dissolved ketone heated to about boiling point of the ketone or of the solvent, to which ketone or solution thereof an oxidation catalyst has been added and which is situated in a vertical long cylindrical vessel provided with a reflux condenser. It is advantageous to disperse the oxidising gas as finely as possible, as for example by employing finely porous glass filter plates (fritted glass particles) and filler bodies, such as shavings or, especially bodies of the kind known as Raschig rings. The reaction vessel is constructed from materials resistant to the components of the reaction and, if necessary, pressure-tight. Such materials are for example ceramic masses, glass or metal alloys such as chrome-nickel steels, or nickel alloys free from iron. Similarly, the filler bodies may be made from the same resisting materials. It is advantageous to add a small amount of an acid, preferably acetic acid, to the ketone at the start, since in this case the reaction commences immediately.

When carrying out the reaction with ketones having a boiling point below the reaction temperature working under increased pressure is necessary in order to keep the ketone in the liquid phase. It is, however, also possible in this case to dissolve the ketone in a solvent having a higher boiling point, such as glacial acetic acid, in which case the reaction may also be carried out at atmospheric pressure, the use of an increased pressure being, however, also possible.

The process proceeds in a particularly advantageous manner when acetic acid together with the catalyst is first introduced into the oxidation vessel, the ketone to be oxidised being introduced gradually into the acetic acid solution or other dispersion while simultaneously leading in oxygen or air. Working in the last-mentioned manner has the advantage that the process may be carried out at temperatures up to the boiling point of the acid employed for dispersing the catalyst without the employment of increased pressure. At the same time the yield is especially favourable. It is preferable to introduce the ketone, the solvent if such be employed, and the catalyst into the vessel and to carry out the oxidation as a batch process.

The waste gas formed during the oxidation contains but a little carbon dioxide and a little aldehyde, such as acetaldehyde which is formed as an intermediate product in the reaction; the gas may be used for further oxidations, if desired,

after washing out the aldehyde and the carbon dioxide, for example with the aid of an aqueous solution of a caustic alkali, such as caustic soda or caustic potash, if desired after separating the aldehyde by cooling.

The following Examples will further illustrate how the said invention may be carried out in practice but the invention is not restricted to these Examples.

EXAMPLE 1.

A mixture of 98 grams of cyclohexanone with 100 grams of glacial acetic acid and 0.1 gram of manganese acetate is introduced into a cylindrical vessel of chrome-nickel steel having an inner diameter of 5.5 centimetres and a height of 35 centimetres and the bottom of which is provided with a porous glass filter. After heating the vessel to about 100° Centigrade a current of air is introduced through the glass filter at the rate of 25 litres per hour. After 5 hours the oxidation is interrupted and the unaltered cyclohexanone is distilled off together with the acetic acid, the distillate being then subjected again to oxidation. Adipic acid is thus obtained in a yield corresponding to 80 per cent of the cyclohexanone employed.

EXAMPLE 2.

A solution of 112 grams of methyl cyclohexanone in 100 grams of glacial acetic acid is oxidised in the manner described in Example 1, after the addition of 0.1 gram of manganese acetate, the reaction temperature being, however, 80° Centigrade. The yield in methyl adipic acid is 74 per cent calculated on the methyl cyclohexanone employed.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is:—

1. A process for the production of dicarboxylic acids which consists in subjecting a cycloaliphatic ketone to oxidation in the liquid phase by means of oxygen or a gas containing oxygen in the presence of oxidation catalysts.

2. The process for the catalytic oxidation of cycloaliphatic ketones substantially as described in each of the foregoing Examples.

3. Dicarboxylic acids when prepared in accordance with the process particularly described and ascertained or its obvious chemical equivalents.

Dated this 7th day of March, 1934.

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Agents.